HCTL Open Int. J. of Technology Innovations and Research
HCTL Open IJTIR, Volume 2, March 2013
e-ISSN: 2321-1814
ISBN (Print): 978-1-62776-111-6

Synthesis and Characterization of ZnO Films on Glass Substrate via Spray Pyrolysis Deposition Technique

Andrea Gracia Cuevas*and Alladin Caballes Jasmin†
andrea.cuevas30@yahoo.com and acjasmin@up.edu.ph

Abstract

Zinc oxide (ZnO) films on glass substrate were synthesized via spray pyrolysis using an aqueous solution of zinc chloride ($ZnCl_2$) as the starting precursor. The experiment was implemented in an atmospheric condition. Different deposition times were used: 5 minutes, 10 minutes, and 15 minutes. It was observed that the films deposited on glass are textured, highly crystalline and c-axis oriented. It was also observed that with increasing deposition time, the thickness of the film increase. The grainy texture of the film exhibit light scattering effect and this affects the film's transparency.

*Department of Physical Sciences, College of Science, University of the Philippines at Baguio City, Philippines
†Department of Physical Sciences, College of Science, University of the Philippines at Baguio City, Philippines

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Keywords

Zinc Oxide, Thin Films, Spray Pyrolysis, Zinc Chloride, Chemical Synthesis

Introduction

ZnO is an important basic material for various applications due to its low cost as well as its electrical, optoelectronic and luminescent properties [1]. Zinc oxide has been also used for its anti-bacterial, photocatalytic and gas sensing properties [2]-[4]. There are a number of ways to fabricate ZnO thin films and one of these is through spray pyrolysis. This method involves heating up the substrates prior the deposition and such would be essential for a reaction to occur and a thin solid film would be deposited. This method has been widely used because of its uninterrupted deposition process, efficiency, cost-effectiveness [5]-[7]. This has been successfully used to fabricate oxide thin films. Such materials have been used for electronic devices. Many researchers have worked with $ZnCl_2$ as precursor to fabricate doped and undoped ZnO films, nano and microstructures, because metal chloride salts can be used to implement spray pyrolysis [1]-[2], [7]-[10].

This study involves the fabrication of ZnO films using a cost-efficient, simple, and effective technique - spray pyrolysis - using a commercial sprayer. Scanning electron microscopy and X-Ray diffractometry are used for the analysis of the surface morphology, microstructure and crystallinity of the films. UV-Vis spectrophotometer is used for optical characterization of the films.

Experimental Details

A spray pyrolysis system was constructed using a commercially available sprayer as the precursor atomizer, and a hotplate as the heating apparatus for the substrate. 0.1M aqueous solution of $ZnCl_2$ was used as precursor. Glass slides were used as substrates, with 0.9 cm x 3.8 cm as its dimensions. The substrates were cleaned using standard sample preparation procedure. The cleaned substrates were then heated up to 400^o C prior to deposition. Different deposition times were implemented for the experiment: 5 minutes, 10 minutes, and 15 minutes. The deposition was pulse-sprayed, with one spray for every 5 seconds. The nozzle-substrate distance was fixed at 37.5 cm. The deposition was done in ambient air.

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The crystal phase of the as-deposited films is analyzed by x-ray diffractometer (XRD) with $CuK\alpha$ radiation ($\lambda = 1.54$ Å). The ZnO phase was indexed using the JCPDS files. The surface morphology and thickness of the films are obtained by scanning electron microscopy (SEM model Phillips 30 XL Field Emission Gun), operated at 5 kV. The optical transparency of the films was measured using Shimadzu UVmini-1240 UV-Vis spectrophotometer.

Results and Discussion

The surface morphology of the films is shown in figure 1. It can be observed that the surface texture of the films changes with increasing deposition time. Figure 1(a) shows the appearance of randomly oriented thin flakes with 1 μm dimension. In figure 1(b), globular grains (with 0.19 nm - 0.72 nm grain size) seem to nucleate on top of the thin flakes initially deposited. The grain density increases with increasing deposition time as shown in figure 1(c). The grains from the films deposited for 15 minutes have a size range from 0.19 nm to 0.79 nm.

It is known that using $ZnCl_2$ as precursor, a non-uniform surface morphology

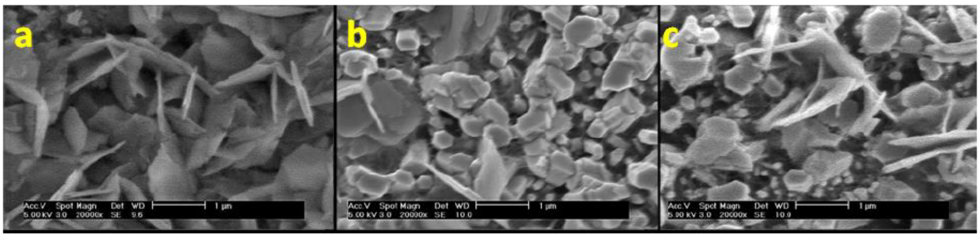

Figure 1: *SEM micrographs of ZnO deposited on glass with deposition times of (a) 5 minutes, (b) 10 minutes, and (c) 15 minutes.*

and prominent grain boundaries can be clearly observed from the surface of the film [1, 8]. Due to the high dissociation enthalpy of $ZnCl_2$, the droplets are not easily dissociated, which means the nucleation requires less energy [13]. Due to the low surface tension of $ZnCl_2$, it favours the droplet spreading, which results to more diffused nucleation sites [8]. Thus, more textured or grainy film is formed.

Formation of aggregates or grains could be obtained from strong interaction between particle and substrate, which would result to a less compact and ran-

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domly oriented structure [8]. The surface roughness of the substrate which is glass could be accounted for the presence of aggregates in the films.

Figure 2 shows the SEM micrographs of the cross section of films deposited for various times. Both films show uneven thickness. This is due to the diverse surface morphology as shown in figure 1. Film thickness is measured by taking four (4) representative spots for each image. The film thicknesses obtained for the films deposited at 10 minutes and 15 minutes are 1.581 microns and 1.884 microns, respectively. For the film deposited for 5 minutes, no thickness mea-

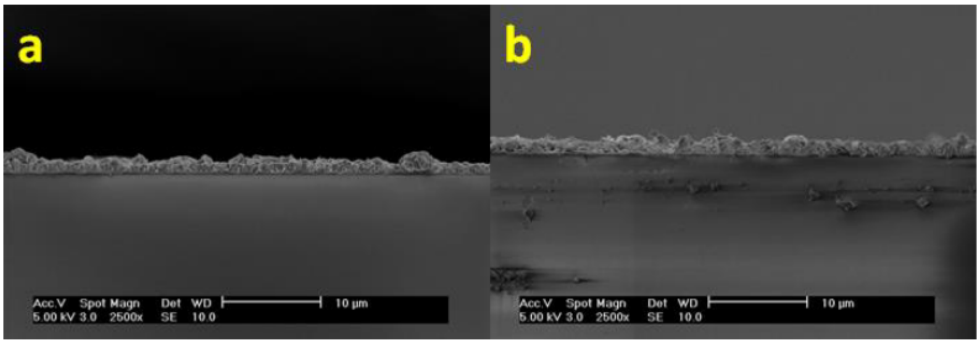

Figure 2: *SEM micrographs of the cross section of films deposited for (a) 10 minutes, and (b) 15 minutes.*

surement could be acquired. This could be accounted from the low nucleation of ZnO globular grains. The film deposited for 5 minutes is mostly composed of thin flakes, which are too small and highly dispersed to be used for thickness measurement. For deposition times greater than 5 minutes, ZnO particles start to nucleate on top of the thin flakes. This makes the film to be composed globular grain aggregates. During this time, the ZnO globular particulates fuse on top of the other, hence the abrupt increase in thickness of the material for deposition time greater than 5 minutes.

Figure 3 shows transmittance of ZnO films deposited on glass substrate for the three deposition times. It can be observed that the transmittance of the films decreases with increasing deposition time.

In the wavelength spectrum of 400 nm to 700 nm, film (a) has a transmittance range between 0.06 and 0.30. Film (b) has a transmittance range between 0.01 and 0.15 while film (c) is between 0.01 and 0.12. Films (b) and (c) have significantly lower transmittance as compared to film (a). The decreased

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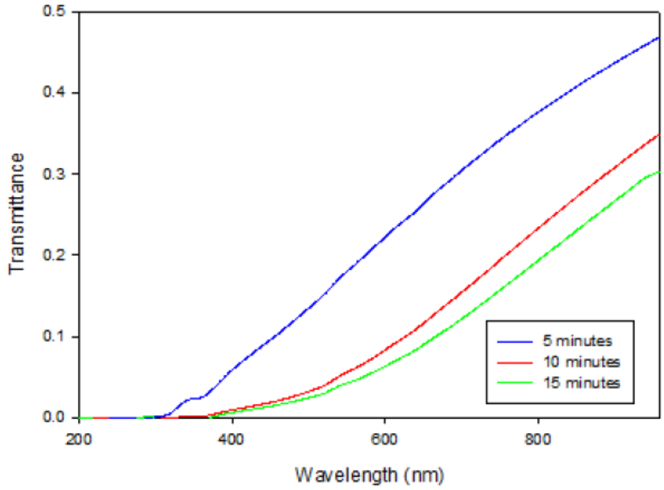

Figure 3: *Transmittance spectra of ZnO deposited on glass for (a) 5 minutes, (b) 10 minutes, and (c) 15 minutes.*

transmittance of the films might be due to the light scattering at the grain boundaries [11]. The presence of grains, as shown in figure 1, for the films deposited for 10 and 15 minutes could have increased the light scattering, hence the decrease in optical transmittance. Moreover, the film thickness, due to vertical stacking of grains, also increases the film's opacity.

Figure 4 shows the XRD spectra of films deposited for 5 minutes and 10 minutes. There is a sharp peak at a Bragg angle of 34.72^o. This diffraction peak is indexed as (002) plane of the ZnO film with hexagonal wurtzite crystal structure. This is also consistent with previous results indicating that the ZnO films preferentially grow along the c-axis [12]. It can also be observed that no impurity phases can be seen in the XRD spectrum. In addition, the intensity of the (002) peak is higher for the films grown for 15 minutes as compared to the film grown for 5 minutes. This can be attributed to larger amount of ZnO materials in the sample as depicted by the thickness measurement of the ZnO sample.

The spray pyrolysis technique used in this study produces quality ZnO films. Although the film thickness affects the transparency of the films, the crystallinity of the film is not significantly affected. The formation of globular aggregates makes the film highly textured and the grain boundaries become more prominent. However, this makes the ZnO films of good use in adsorption,

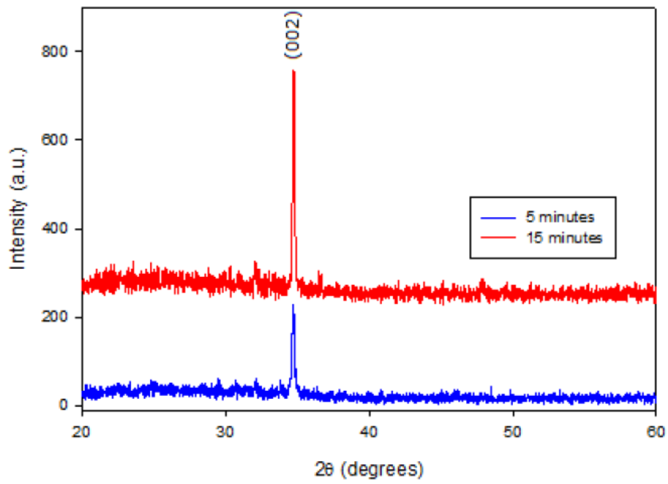

Figure 4: *XRD Spectra of films deposited on glass for 5 minutes and 15 minutes.*

gas sensing and antibacterial applications [4].

Conclusions

Textured films of ZnO were successfully synthesized using spray pyrolysis method. The films show good transparency in the visible light spectrum. The thickness of the film affects the transparency due to the increase of light scattering from grain aggregates. Results from the XRD data show that the ZnO films are of wurtzite structure and have c-axis preferential growth. The ZnO films also exhibit high crystallinity and high phase purity.

Acknowledgements

This research is funded by the National Research Council of the Philippines. The authors would also like to thank the National Institute of Materials Science, Tsukuba, Japan for the XRD characterization through the efforts of Dr. Alipio Garcia and Dr. Chelo Pascua.

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